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Oxidative(anodic) treatment of glassy carbon(GC) in aqueous alkaline media was found to cause the formation of a unique mesa morphology. Injection of some species (perhaps OH<sup>-</sup>) below the surface with attendant volume change was suspected to be the cause for the peculiar morphological change. The present paper reports the mechanism of the mesa formation and its application to enhance the catalytic activity for electropolymerization of conducting polymers and the double-layer capacitance of the resulting polypyrrole/GC film.

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# Morphology Changes due to Oxidative Treatment of Glassy Carbon Electrodes and Its Applications

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## Introduction

Glassy carbon (GC) is a popular electrode material in electrochemistry due to its inertness; however like other carbonaceous material it can be also used as a catalyst. Electrochemical pretreatment (1-3), as well as other forms of surface oxidation, including oxygen plasma treatment (4), have already been used to improve the electrocatalytic behavior of GC for subsequent electrochemical reactions. For example, the reduction of oxygen on GC has been shown to increase upon anodic treatment (5). Also, with the introduction of carbon layers as a protective overcoat for thin-film magnetic media, the study of carbonaceous material is gaining additional importance.

Electrochemical treatment of GC was found to cause the formation of a unique mesa morphology. Injection of some species below the surface was suspected to be the cause for such a dramatic morphology change.

## Experimental

GC rotating disk electrodes were used throughout this study. The GC disks (0.645 cm in diameter) were carefully polished with alumina (0.3 and 0.05  $\mu\text{m}$  in diameter) on a metallography wheel.

For the anodic treatment of GC, a platinum electrode was used as a counter electrode. The potentials were referred to SCE and the electrolyte solution was 1.0 mol  $\text{dm}^{-3}$  NaOH(aq). The GC was treated by applying a constant potential pulse in the range of 1.5 - 2.6 V for different exposure times in order to grow mesas on the smooth substrates. Ex-situ studies were done on GC samples using Phase Detection Interferometric Microscopy (PDIM) or Scanning Electron Microscopy (SEM) to follow the morphology changes.

## Results and Discussion

Oxidative treatment of GC electrodes in alkaline solution resulted in the formation of mesas as shown in Fig. 1. Figure 1 reveals that original scratches on the surface extend across the top of the mesa and continue on either side. Since the mesa has grown from within the GC and has raised the original scratch, its formation is not merely a surface phenomena.

At a given voltage, the first mesas to appear were all at the edge of the electrode. As treatment continued, more and more mesas were formed in the center of the GC electrode. Therefore the number of mesas increased with time of exposure. At any given time, however, the overall surface density of the mesas was higher at the edge of the electrode and decreased toward the center. Higher current density at the edge was assumed to be the cause for this behavior.

A threshold time was discovered before which no mesas were observed on the surface. Figure 2 indicates that at lower voltages, the threshold time increases. A threshold voltage of approximately 1.5 V was determined, below which mesas could not be formed even for extended exposure.

At a given voltage, the height of the mesas increased with duration of treatment. The base area of the mesas on the other hand did not increase with time. At 2.0-2.6 V, most mesas were 20-60  $\mu\text{m}$  in diameter. At lower voltages the mesas were of smaller diameter.

Although repolishing the samples removed the mesas, oxidative treatment regenerated them, indicating the reproducibility of the mechanism. However the mesas were not generated at the same location each time. Reductive (cathodic) treatment of GC in either basic (NaOH) or acidic ( $\text{H}_2\text{SO}_4$ ) solution did not cause the shrinkage or collapse of the mesas suggesting an irreversible process.

Activation of GC in NaOH solutions is accompanied by changes of surface morphology, most importantly formation of mesas. Intercalation of species such as alkali metal ions and  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  anions into graphite (6) and GC (7) has been noted previously. We propose that in our experiment some species (perhaps  $\text{OH}^-$  ions) were injected below the surface causing localized buildup of stress, swelling, and the formation of mesas. The presence of graphitic regions in the GC is proposed to be crucial in the injection process.

The authors will discuss about the mechanism of mesa formation and the enhancement of its catalytic activity. The emphasis of the present paper is to investigate electrochemical activity changes of the GC surface that accompanied by the oxidative (anodic) treatment in alkaline solution. As one of the applications of an anodic treated GC, the enhancement of the catalytic activity for electropolymerization of conducting polymers as well as their double layer capacitance will be discussed.

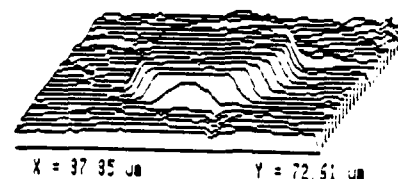


Fig. 1 PDIM images of GC surface after anodic treatment.

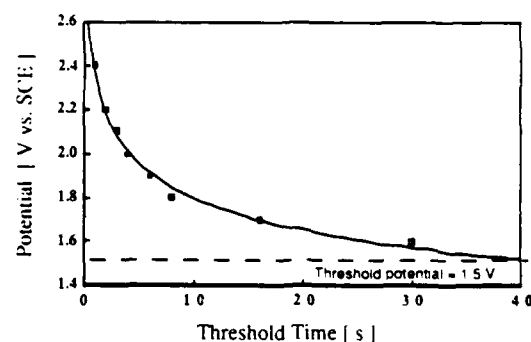


Fig. 2 Plot of applied potential vs. threshold time for anodic treatment of GC in 1 mol  $\text{dm}^{-3}$  NaOH(aq).

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